Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27060

221 (2021) 218–228
May

Cadmium removal from aqueous solution using cellulose nanofibers obtained from waste sugarcane bagasse (SCB): isotherm, kinetic, and thermodynamic studies

Mahboobeh Dehvari[a], Behzad Jamshidi[a,b,*], Sahand Jorfi[c,*], Sudabeh Pourfadakari[d], Zahra Skandari[e]

[a]*Student Research Committee, Department of Environmental Health Engineering, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran, Tel. +989171506432; emails: behzadjamshidi65@yahoo.com (B. Jamshidi), mahboobehdehvari@yahoo.com (M. Dehvari)*
[b]*Department of Environmental Health Engineering, Petroleum Industry Health Organization, NIOC, Ahvaz, Iran*
[c]*Department of Environmental Health Engineering, Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran, Tel. +989163109153; email: sahand369@yahoo.com*
[d]*Systems Environmental Health and Energy Research Center, The Persian Gulf Biomedical Sciences Research Institute, Bushehr University of Medical Sciences, Bushehr, Iran, email: porfadakar@gmail.com*
[e]*Department of Environmental Health Engineering, School of Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran, email: zeskandari1392@gmail.com*

Received 10 March 2020; Accepted 14 January 2021

ABSTRACT

The aim of this study was to investigate the adsorption of cadmium (Cd) from aqueous solutions using the cellulose nanofibers (CNF) obtained from sugarcane bagasse (SCB). The impact of operational parameters including pH, contact time, adsorbent dosage, and initial cadmium concentration were investigated according to the one-factor-at-a-time method. The results showed that the Cd removal (%) increased in the pH range of 3–5 and remained steady up to pH 6. The maximum adsorption efficiency (99.9%) was obtained at an adsorbent dosage of 4 g/L, pH = 5, Cd concentration of 5 mg/L, and equilibrium time of 70 min. In addition, Cd removal followed the Freundlich isotherm (R^2 = 0.991 at 303°K) and pseudo-second-order kinetic model (R^2 = 0.997). All $\Delta G°$ values were negative and the positive values of enthalpy change ($\Delta H°$ = 66.76 kJ/mol), and entropy change ($\Delta S°$ = 0.238 kJ/mol) showed that the adsorption process of Cd(II) was endothermic and spontaneous. With regards to the reliability and efficiency of CNF, this adsorbent is recommended for the removal of heavy metals such as Cd from an aqueous environment.

Keywords: Sugarcane bagasse; Cellulose nanofiber; Cadmium; Adsorption; Water treatment

1. Introduction

Heavy metals are advantageous in industry, but they also have unfavorable impacts on the environment and humans. These metals are resistant to biodegradation and can be accumulated in living organisms [1]. Cadmium (Cd) is one of the heavy metals that is known as a major environmental pollutant [2]. The high concentrations of Cd may exist in aqueous solutions due to the discharge of industrial wastewater and leakage of Cd compounds from the pipes coated with it. Cd is used in industries such as electroplating, rechargeable nickel–cadmium batteries, the control rods of nuclear reactors, pulp, and paper [3,4]. Therefore, it is discharged into the environment and causes serious environmental and health problems. Cd has been reported to be toxic to humans and animals and it is

---

* Corresponding authors.

1944-3994/1944-3986 © 2021 Desalination Publications. All rights reserved.

known to be carcinogenic [5,6]. The maximum permissible level of cadmium in drinking water is 0.005 mg/L and the tolerance limit for Cd discharge into surface waters is 2 mg/L [7]. Therefore, Cd removal from water resources and industrial wastewater is necessary.

Different techniques are used for Cd ions removal from industrial wastewater including phytoremediation [4], chemical precipitation [8], ion exchange [9], and reverse osmosis [10]. These methods have difficulties such as high energy demands, incomplete removal of pollutants, high costs, and production of sludge or other toxic wastes that must be managed. Following these reasons, efficient, cost-effective, and environment-friendly methods such as biosorption technologies are developed to remove heavy metals [11,12]. Recently, more attention has been paid in the field of adsorption by agricultural solid wastes such as the orange peel [13], pomegranate seed [14], acroptilon repense flower powder [11], and palm oil mill sludge biochar [15].

Every year around 54 million tons of bagasse are produced in the world [16]. The sugar industry is generating huge amounts of bagasse as a waste product. In Iran, approximately 4.3 million tons of sugarcane bagasse (SCB) is produced annually, mainly in southwest province Khuzestan [17,18]. About 50% of SCB is composed of cellulose and the rest is hemicellulose and lignin. According to researches, the cellulose content of SCB is higher than many other agricultural wastes [19]. Various modification techniques were investigated on the cellulose extracted from SCB such as chemical treatment using acid or alkali to change the surface of cellulose [18,20–22]. The treatment or modification of lignocellulosic materials leads to the increase of adsorption capacity of these materials and the concentration of the binding sites in bagasse. Cellulose nanofibrils (CNF) are one of the three main groups of nanocellulose that originate from agricultural wastes. The natural and modified SCB is used as adsorbent to remove various pollutants. As yet, the cellulose nanofibril derived from SCB has not been studied as a cadmium adsorbent. In this study, the cellulose nanofibers (CNF) obtained from waste SCB (modified with alkali solution) were used as a new biosorbent for Cd(II) removal from aqueous solutions, and the effect of different parameters on the adsorption process were evaluated.

2. Experimental

2.1. Materials

The SCB used in this study was obtained from the sugarcane farms located in the south west of Iran. Sodium chlorite ($NaClO_2$), cadmium nitrate salt ($Cd(NO_3)_2{\cdot}4H_2O$), acetic acid (CH_3COOH), acetone, dimethylsulfoxide (DMSO), sodium sulfite, and other chemicals were purchased from Merck Company (Germany) and were used without additional treatment.

2.2. Preparation of CNF

Synthesis of CNF was according to the method given by Mandal and Chakrabarty [23]. At first, SCB was collected, sorted, and washed with distilled water several times, then dried in sunlight. In the next step, SCB was ground into parts (5–10 mm) and crushed into small fibers and passed through a 60-mesh screen. The treatment was performed to purify the cellulose by removing lignin and hemicellulose from the SCB fibers. The ground bagasse was treated with sodium chlorite solution 7% (w/v) (ratio of fiber to liquor 1:50) and the pH was adjusted by adding 5% acetic acid solution as the buffer at pH 4, the solution was boiled for 5 h at 323 K, then the solid substance was filtered and washed several times using distilled water. The mixture obtained was boiled for 5 h with 250 mL of sodium sulfite solution 5% (w/v) and thereafter was washed with distilled water. The bleaching process was completed by adding 250 mL of sodium hydroxide solution 17.5% (w/v) to the mixture and was boiled for 5 h. Then at the point of pH neutralization, the solution was filtered with distilled water and was dried in sunlight. 50 mL DMSO was added to the residual material and was boiled in 353 K temperature for 3 h. The mixture was allowed to cool and was filtered using distilled water, the hydrolysis material was centrifuged at 5,000 rpm for 10 min. The centrifugation was repeated several times by adding distilled water, until the pH was fixed at the range of 5–6. At the end, the suspension was sonicated (Hielsccher: UP 400S, Germany) for 5 min in an ice bath, then was kept in refrigeration at 277 K before further use (Fig. 1).

2.3. Experimental procedure

This research was carried out at a laboratory scale in a batch system. To perform the experiments, laboratory jars (250 mL) were used. In addition, hydrochloric acid (0.1 N) and sodium hydroxide (0.1 N) were used in order to adjust the pH level. The stock Cd(II) solution of 500 mg/L was prepared by dissolution of cadmium nitrate salt ($Cd(NO_3)_2{\cdot}4H_2O$) in distilled water. The other solutions were daily prepared from the stock solution. The effect of the different parameters such as pH (3–7), reaction time (0–90 min), initial Cd concentration (5–80 mg/L), temperature (293–313 K), and adsorbent dosage (0.5–5 g) on Cd removal were investigated according to the one-factor-at-a-time method. Mixing was performed using a shaker incubator with 150 rpm. To determine the residual concentration of Cd at the end of the equilibrium time, the samples were centrifuged at 4,000 rpm for 5 min, and the amount of Cd ion in the solution was determined using flame atomic adsorption spectrometer (FAAS) (model AAS vario6 Jena, Germany). The Cd concentration was determined according to the standard methods [24]. The amount of Cd adsorbed by the adsorbent (mg/g) and adsorption efficiency (%) were obtained using Eqs. (1) and (2) [11,25,26]:

$$q_e = \frac{\left(C_0 - C_t\right)V}{M} \tag{1}$$

$$\text{Re}\left(\%\right) = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \tag{2}$$

where C_0 and C_t are the initial and final concentration of Cd in solution, q_e is the amount of Cd adsorbed (mg/g), V is the volume (L), M is adsorbent dosage (g), and Re is the removal efficiency.

Fig. 1. Images of sugarcane bagasse (a) before and (b) after modification.

2.4. Characterization of adsorbent

The scanning electron microscopy (SEM) technique by a 10 kV HITACHI S-4800 NIHE SEM (Japan) was used to examine the surface texture and morphology of the adsorbent. Surface functional groups in the adsorbent structure were determined by using Fourier transform infrared spectroscopy (FTIR, PerkinElmer-RX1 FT-IR system, USA). The determination of surface area and porosimetry with nitrogen gas adsorption was carried out using the Micromeritics (ASAP 2010, Norcross, USA) analyzer [1,21,27]. The elemental analysis of adsorbent is one of the parameters for explaining the mechanism and behavior of the adsorption process. The C, H, O, and N contents of the adsorbent were determined using the costech ECS 4010 CHNSO analyzer.

2.5. Desorption study

Desorption of metal ions from the loaded CNF was carried out using desorbing agents (HCl, HNO_3). For the desorption study, the CNF isolated from the solution was submerged in the HCl and HNO_3 (0.5 M) solutions and was placed on a shaker incubator at 150 rpm for 70 min at 298 K [28]. The experimental adsorption–desorption was conducted at four cycle. Desorption ratio (DR%) was calculated through Eq. (3) [29,30].

$$\text{DR\%} = \frac{\text{Amount of desorbed metal ion}}{\text{Amount of adsorbed metal ion}} \tag{3}$$

2.6. Adsorption isotherms

To describe the mutual behavior of the adsorbent and the adsorbate and to predict the adsorption capacity of the adsorbent, the Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin isotherm models were investigated. The experiments were performed in different concentrations of Cd at the temperature of 303 K and the contact time of 70 min. Equations as well as the linear forms of these isotherms are presented in Table 1 [31,32].
where q_e is the adsorption equilibrium capacity (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), K_L is Langmuir constant related to adsorption capacity (L/mg), Q_m is the maximum adsorption capacity (mg/g), K_f is the adsorption capacity (L/mg), $1/n$ is

Table 1
Isotherm models

Type of isotherm	Equation	Linear form	Eq. No.
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e$	(4)
Langmuir	$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_m}\right) + \left(\frac{1}{Q_m}\right) C_e$	(5)
Temkin	$q_e = B_1 \ln\left(K_T C_e\right)$	$q_e = B_1 \ln K_T + B_1 \ln C_e$	(6)
D–R	–	$\ln q_e = \ln q_m - \beta\varepsilon^2$	(7)

Table 2
Kinetic models

Type of kinetic	Equation	Eq. No.
Pseudo-first-order	$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t$	(8)
	$\frac{dq_t}{dt} = K_1(q_e - q_t)$	(9)
Pseudo-second-order	$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$	(10)
	$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$	(11)

the adsorption intensity. B is Temkin constant which is related to the heat of sorption (kJ/mol), K_T is Temkin isotherm constant which shows the maximum binding energy (L/mg), β is the activity coefficient useful in obtaining the mean sorption energy (kJ/mol), ε is Dubinin–Radushkevich constant.

2.7. Adsorption kinetics

In order to assess the adsorption process of Cd on CNF, pseudo-first-order and pseudo-second-order models were used. The equations of these kinetics are presented in Table 2 [12,33,34]:
where q_e is the adsorption equilibrium capacity (mg/g), q_t is the amount of Cd adsorbed at time t (mg/g), K_1 is the rate constant of pseudo-first-order (min^{-1}), and K_2 is the rate constant of pseudo-second-order (g/mg min). These parameters were obtained from slope and intercept of pseudo-first-order and pseudo-second-order plots between $\log(q_e - q_t)$ vs. t and t/q_t vs. t.

2.8. Thermodynamic study

Thermodynamic parameters such as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$), and entropy change ($\Delta S°$) can discern whether the process is spontaneous or not. The negative values of $\Delta G°$ show a spontaneous process and the value of enthalpy change ($\Delta H°$) shows the exothermic or endothermic nature of the adsorption process, and the difference between physical and chemical adsorption processes. The temperatures used in the thermodynamic study were 293–313 K. The thermodynamic parameters were calculated as following [35,36]:

$$\Delta G° = -RT\ln(K_L) \tag{12}$$

$$\ln(K_L) = \left(\frac{\Delta S°}{R}\right) - \left(\frac{\Delta H°}{RT}\right) \tag{13}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{14}$$

where K_L is the equilibrium constant, R is the universal gas constant (8.314 J/mol k), T is the temperature (°K), and $\Delta S°$, $\Delta H°$ were determined by using Van't Hoff equation.

3. Results and discussion

3.1. Characteristics of the SCB

The SEM images of SCB before modification are presented in Figs. 2a and b. The surface of the unmodified SCB has been covered by impurities and residual of lignin. The approximate crystallite size of SCB was found in the range of 17.86–49.13 nm.

Figs. 2c and d indicates the SEM images of SCB after modification. Modification with sodium hydroxide results in the removal of most of the lignin. As can be seen, the sample had porous structure and overlapping fiber layers which are responsible for physical adsorption. The small fragments on the adsorbent surface indicate the potential possibility of cadmium adsorption. Also, it is obvious that the cellulose fibers obtained after the modification contain nano-sized particles mostly in the range of 22.33–84.85 nm.

The FTIR spectra of the modified SCB is presented in Fig. 2e. FTIR spectra indicate the absorption peaks around 620; 1,619; and 3,400–3,470 cm^{-1} that are related to hydroxyl and carbonyl groups and esters that have an important role in the Cd adsorption. The functional groups decreased after modification. The FTIR results show that chemically activated SCB had some functional group changes that lead to higher adsorption capacities of chemically treated adsorbent [21].

As shown in Table 3, the surface area of the modified SCB was 1.8614 m^2/g. Since the mean pore diameter is 9.4775 nm, thus the adsorbent has a mesopore structure. The maximum value of the relative pressure (P/P_0) reached 0.990. Desorption relative pressure values are related to a more stable thermodynamic condition. According to Fig. 3, the proportional increase was observed in the volume (V_a) of nitrogen atoms on the surface of the sample.

Table 4 shows the results of the elemental analysis of the unmodified and modified SCB. The carbon content of unmodified and modified SCB was 59.46% and

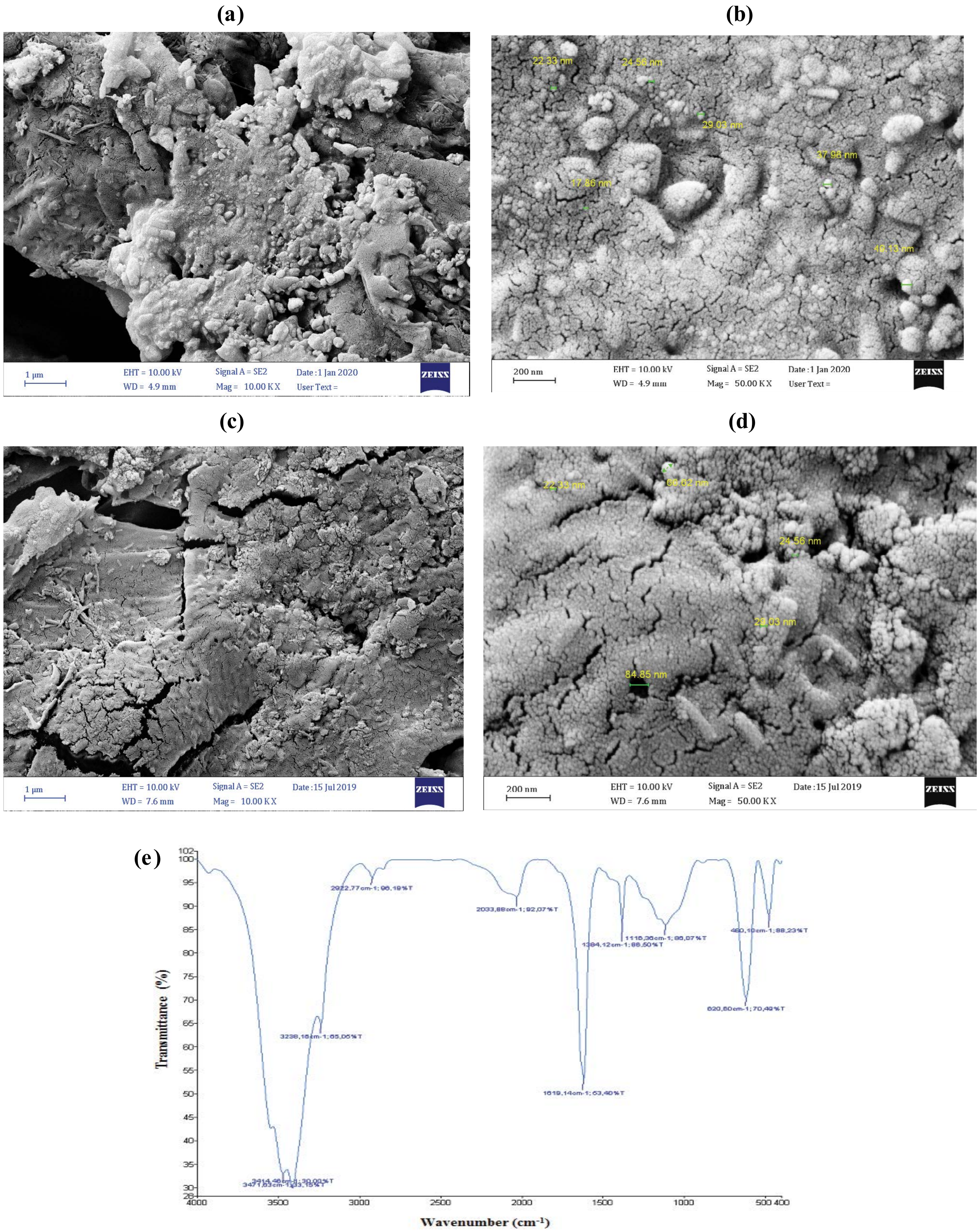

Fig. 2. (a and b) SEM images of unmodified sugarcane bagasse, (c and d) SEM images of modified sugarcane bagasse, and (e) FTIR spectra of modified sugarcane bagasse.

Table 3
Characteristics of the porosity of modified sugarcane bagasse

Parameter	Value
Correlation coefficient	0.9987
V_a (volume of pores), cm^3/g (STP)	0.4277
S_{BET} (superficial area), m^2/g	1.8614
Total pore volume (P/P_0 = 0.990), cm^3/g	0.0044103
Mean pore diameter	9.4775

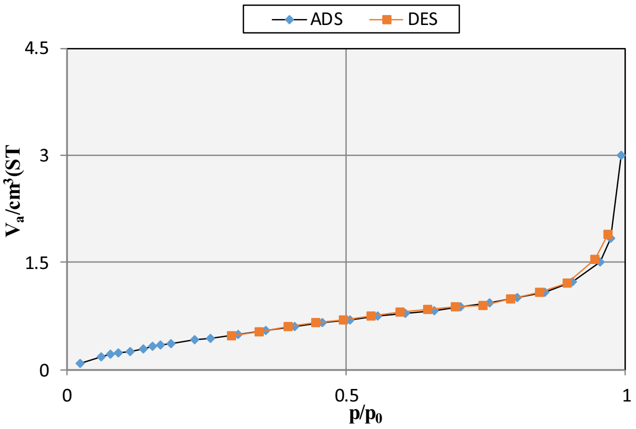

Fig. 3. Adsorption and desorption isotherms in nitrogen gas for the modified sugarcane bagasse.

Table 4
Elemental analyses of the unmodified and modified sugarcane bagasse

Element	Unmodified (wt.%)	Modified (wt.%)
C	59.46	58.41
O	33.95	33.52
H	6.10	6.93
N	0.49	1.14
S	–	–

56.43%, respectively. The SCB is a suitable absorbent for the removal of pollutants due to its high quantity of carbon.

3.2. Cd adsorption

3.2.1. Effect of pH

The pH of the solution is one of the important parameters in the adsorption processes that affects the surface charge of the adsorbent and the degree of the ionization of the adsorbate [37]. The results of the pH effect on the removal efficiency of Cd(II) ion are shown in Fig. 4. As can be seen, with increasing pH from 3 to 5, the removal efficiency was increased from 44.9% to 60% at 90 min. At pH = 7 and 90 min, the removal efficiency decreased to 41%.

According to the results, removal efficiency decreased at pH < 5 and pH > 5. In deionized water, different species of Cd exist depending on the pH of the solution. At pH < 6, Cd^{2+} ion is the dominant species present in the solution. At acidic pH, excess H^+ ions compete with Cd^{2+} ions for the adsorption sites and decrease the removal efficiency. At higher values of pH, negative charge sites increase on the adsorbent surface that creates an electrostatic attraction force between the adsorbent and the metal ion. In addition at pH > 5, soluble hydroxyl groups $(Cd(OH)^+)$ are formed that reduces the adsorption of Cd by the CNF [38–41]. The obtained results are consistent with other studies done by researches such as Cheraghi et al. [39] and Hamidpour et al. [41]. According to the results, pH = 5 was selected as the optimum pH.

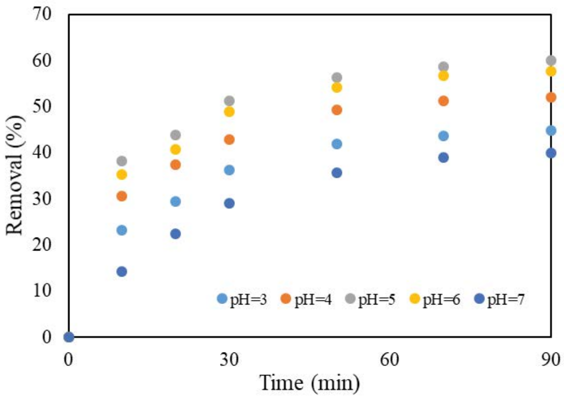

Fig. 4. Effect of pH on the removal efficiency of Cd(II) (CNF dosage: 1 g/L, initial Cd(II) concentration: 50 mg/L).

3.2.2. Effect of CNF dosage

Effect of CNF dosage on Cd(II) ion removal is shown in Fig. 5. According to the results, by increasing CNF dosage from 0.5 to 5 g/L at 10 min time, the removal efficiency increased from 20.4% to 64.7%, respectively. These values were 41.9% and 93.4% at 70 min, respectively. As the adsorbent dosage increases, the number of the sites available for Cd bonding to the adsorbent increases and as a result, the removal efficiency increased. Afroze and Sen [1] studied the heavy metal ions adsorption from water by agricultural solid waste adsorbents. The results of these researches showed that higher adsorbent dosage leads to higher removal efficiency. This could be attributed to the increase in surface area and increasing the number of active binding sites on the adsorbent. Since the removal efficiency was not significantly different between adsorbent doses 4 and 5 g/L, adsorbent dosage 4 g/L was chosen as the optimum level.

3.2.3. Effect of the initial Cd concentration

According to the obtained results (Fig. 6), the removal efficiency decreased as the initial cd concentration increased. By increasing metal concentration from 5 to 80 mg/L, the removal efficiency decreased from 99.9% to 70.1%. At low concentrations due to high specific surface area and quicker adsorption of adsorbent by adsorption sites, metal ions can interact with the adsorption positions on the adsorbent surface and so the removal efficiency increases. At higher concentrations due to the saturation of

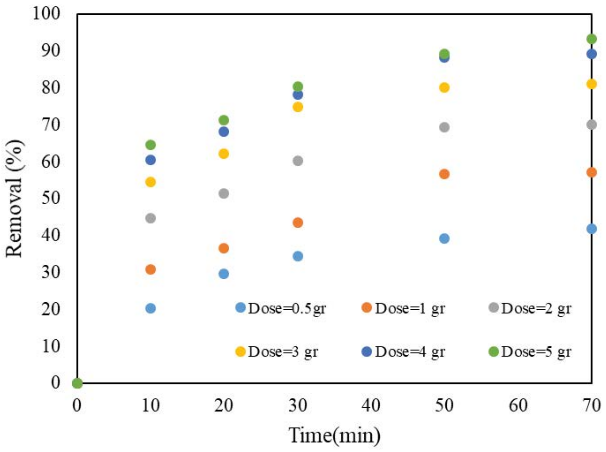

Fig. 5. Effect of CNF dosage on the removal efficiency of Cd(II) (pH: 5, initial Cd(II) concentration: 50 mg/L).

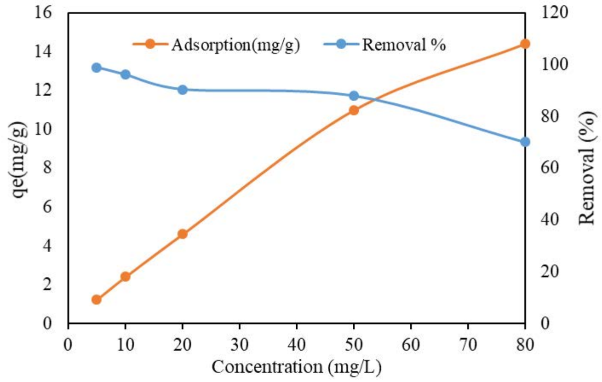

Fig. 6. Effect of the initial Cd(II) concentration on the removal efficiency of Cd(II) (pH: 5, CNF dosage: 4 g/L, and contact time: 70 min).

adsorption sites, the removal efficiency decreases. Afroze and Sen [1] and Pham et al. [20] achieved similar results.

The results showed that with enhancing the concentration, adsorption capacity (q_e) increased from 1.23 to 14.42 mg/g. The study results of Garg et al. [38] showed by increasing the metal ion concentration from 5 to 500 mg/L, adsorption capacity increased from 0.24 to 6.75 mg/g. These researchers stated that this is due to the increased rate of mass transfer because of the built up concentration of the driving force.

3.3. Isotherm studies

It is important to determine the isotherm models in order to optimize the adsorption system for adsorption of the adsorbed material. In the present study, the Langmuir, Freundlich, Temkin, and D–R isotherms were investigated. The values of isotherm constants and correlation coefficients were calculated and are listed in Table 5. For investigation of the best isotherm model, the correlation coefficient and parameters of R_L (Langmuir isotherm) and $1/n$ (Freundlich isotherm) were considered as indicated below [1,14,42]:

Table 5
Results of the isotherm calculations

Type of isotherm	Isotherm parameters	
Langmuir	q_m (mg/g)	20
	K_L (L/mg)	0.44
	R_L	0.77
	R^2	0.988
Freundlich	$1/n$	0.456
	K_F (mg/g)	4.85
	R^2	0.991
Temkin	B_T (kJ/mol)	1.36
	K_T (L/mg)	5.43
	R^2	0.916
D–R	q_m (mg/g)	19.88
	E (kJ/mol)	16.6
	R^2	0.698

$R_L > 1$: unfavorable; $R_L = 1$: linear; $0 < R_L < 1$: favorable; $R_L = 0$: irreversible.

$1/n = 1$: linear; $1/n < 1$: favorable; $1/n > 1$: unfavorable.

R_L is the separation factor that is calculated according to the following equation:

$$R_L = \frac{1}{\left(1 + K_L C_0\right)} \tag{16}$$

According to the results, the experimental data followed the Freundlich isotherm model (Fig. 7). The correlation coefficient (R^2) value for the Freundlich isotherm was higher than 0.99 ($R^2 = 0.991$). In addition, $1/n$ value was obtained 0.456 (less than 1) that indicates favorable adsorption and suggests that the process was controlled by chemisorption. The experimental data follows the Langmuir isotherm model by the correlation coefficient of $R^2 = 0.988$. R_L parameter was obtained 0.77 that shows the adsorption is favorable ($0 < R_L < 1$). The Langmuir model assumes that the adsorption sites on the adsorbent are homogeneous. Therefore, according to the results, it can be concluded that the adsorption mechanism is a combination process of the physical and chemical monolayer adsorption.

R^2 value of Temkin isotherm ($R^2 = 0.916$) was lower than the Langmuir and Freundlich isotherm models. The D–R isotherm had a low correlation coefficient ($R^2 = 0.698$). The heat of adsorption (B) in Temkin isotherm indicates the type of the adsorption (physical or chemical adsorption). So that if $B < 40$ kJ/mol, it is physical adsorption, and if $B > 40$ kJ/mol, the adsorption is chemical. According to the results, B-value is equal to 1.36 kJ/mol indicating physical adsorption. The mean free energy of adsorption (E) in D–R isotherm model provides information on the mechanism of absorption. If $E > 8$ kJ/mol, the predominant mechanism of the adsorption process is chemisorption, and if $E < 8$ kJ/mol, the predominant mechanism is physical. In the present study, E is equal to 16.6 kJ/mol, therefore the dominant mechanism of the adsorption process is chemisorption.

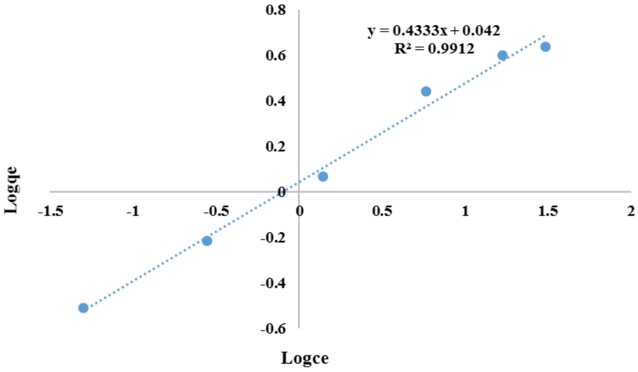

Fig. 7. Freundlich isotherm model for Cd adsorption using CNF (pH: 5, CNF dosage: 4 g/L, and contact time: 70 min).

The present results showed that the Freundlich isotherm is better than the Langmuir, Temkin, and D–R isotherms, based on the values of the regression coefficients. Some researchers have also found similar results. Kumar et al. [42] studied cadmium adsorption on to rice husk. The data fit the Freundlich isotherm model based on the value of the regression coefficient (R^2 = 0.995). The present study results were in contrast to some researchers' studies. Cheraghi et al. [39] investigated the removal of cadmium by Sesame leaf and stem. The results were in good concordance with the Langmuir isotherm model with R^2 = 0.99.

3.4. Kinetic studies

It is important to determine the kinetic models in order to investigate the mechanism of the adsorption processes. In the present study, the pseudo-first-order and pseudo-second-order kinetics were investigated. The results are presented in Table 6.

According to the results (Fig. 8), the adsorption process follows the pseudo-second-order kinetic with a high correlation coefficient (R^2 = 0.997). R^2 value in the pseudo-first-order kinetic is low (R^2 = 0.884). In addition, the theoretical value of q_e ($q_{e,\text{cal}}$) is lower than the experimental data ($q_{e,\text{exp}}$) that indicates the data does not follow the pseudo-first-order kinetic model.

Similar results were also reported by Kumar et al. [42] who studied about cadmium adsorption from aqueous solution onto rice husk. The experimental data agreed with the pseudo-second-order kinetic (R^2 = 0.999). The results of Cheraghi et al. [39] and Hamidpour et al. [41] studies were well described by both the pseudo-first-order and the pseudo-second-order kinetic models.

3.5. Thermodynamic studies

In the present study, thermodynamic parameters such as the free energy, enthalpy, and entropy changes were investigated. The thermodynamic curve for Cd(II) adsorption onto CNF is presented in Fig. 8. The values of ΔH° and ΔS° were determined from the slope and intercept of Fig. 9. The parameters are presented in Table 7.

ΔG° parameter was used for investigation of physical adsorption or chemisorption of process. If ΔG° value

Table 6
Results of the kinetic calculations

Type of kinetic	Kinetic parameters	
Pseudo-first-order	K_1 (min^{-1})	0.06
	$q_{e,\text{cal}}$ (mg/g)	11.96
	$q_{e,\text{exp}}$ (mg/g)	9.375
	R^2	0.884
Pseudo-second-order	K_2 (g/mg min)	0.0075
	$q_{e,\text{cal}}$ (mg/g)	10.77
	$h = K_2q_e^2$ (mg/g min)	0.87
	R^2	0.997

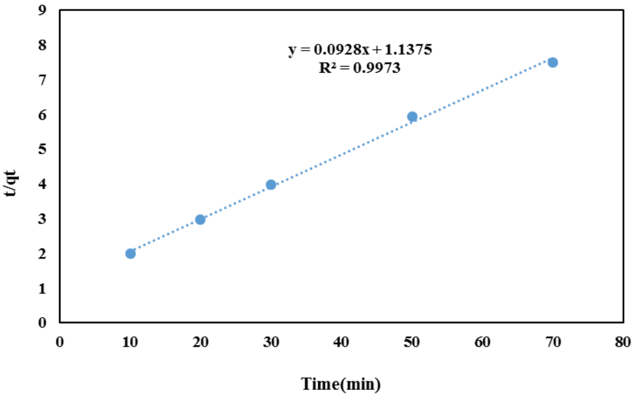

Fig. 8. Pseudo-second-order kinetic model for Cd(II) adsorption using CNF (pH: 5, CNF dosage: 2 g/L, and initial Cd(II) concentration: 50 mg/L).

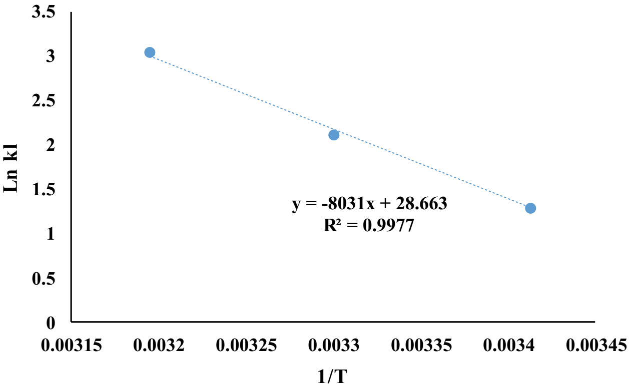

Fig. 9. Thermodynamic curve for Cd adsorption onto CNF (temperature: 293–313 K, pH: 5, contact time: 70 min, CNF dosage: 4 g/L, and initial Cd concentration: 50 mg/L).

Table 7
Thermodynamic parameters

ΔG° (kJ/mol)			ΔS° (kJ/mol)	ΔH° (kJ/mol)
293 K	303 K	313 K		
–26.63	–27.22	–28.12	0.238	66.76

is negative, it means that the adsorption is spontaneous. The negative and positive values of ΔH° indicate that the process is exothermic and endothermic, respectively. The negative value of ΔS° indicates the change in the randomness at the solid/solution interface [1,37,42]. ΔH° value describes the type of adsorption process. The heat of physical adsorption and chemisorption are in a range of 2.1–20.9 kJ/mol and 80–200 kJ/mol, respectively. In the present study, ΔH° was equal to 66.76 kJ/mol that indicates a physico-chemical adsorption process rather than a pure physical or chemical adsorption process.

In this study, the values of ΔS° and ΔH° were 0.238 and 66.67 kJ/mol. The positive value of ΔH° and ΔS° indicates endothermic and randomness adsorption. ΔG° values (up to –20 kJ/mol) indicate that the adsorption process is physical and there is the electrostatic interaction between sorption sites and Cd(II).

3.6. Desorption studies and recyclability

Desorption was evaluated by desorption agents including 0.5 M HNO_3 and HCl. Fig. 10 illustrates the desorption of CNF. The results show that HNO_3 is more effective than HCl. The desorption ratio was reduced after four cycles. So that, in the presence of HNO_3, removal efficiency from 57.1% in the first cycle was decreased to 20.94 % in the fourth cycle. This indicates that it is desirable for use in industries.

3.7. Compare the effect of CFs and CNF

The effect of cellulose fibers (CFs) and CNF on the removal efficiency of Cd is shown in Fig. 11. According to the results, cellulose nanofibers had higher efficiency than cellulose fibers. So that, the removal efficiency in the initial Cd concentration 5 mg/L by CFs and CNF were 85% and 99.9%, respectively.

Nanoscale compounds as an adsorbent have properties such as the small size, the high specific surface, and dominance of interfacial phenomena. CNFs are one of the main families of nanocellulose that are formed of nano-sized thin flexible fibrils with 5–50 nm width and length with the micron scale. The application of CNF as an adsorbent leads to increasing the adsorption capacity, increasing the available ionic sites on which the metal can be bound, and improving the chemical resistance of the adsorbent. This is due to the numerous functional groups (COOH, SO_4^{2-}) formed on the surface of CNFs that facilitate it for creating active surfaces after chemical modification [43,44].

3.8. Comparison of cadmium removal with different adsorbents

The maximum adsorption capacity obtained in this study was compared to reports of other adsorbents. The results are presented in Table 8. The adsorption capacity of Cd(II) using commercial activated carbon was 10.3 mg/g [45]. As regards this process is expensive and difficult to recover, low-cost activated carbons which are also easily available, have attracted the attention of researchers. As can be seen, the adsorption capacity of the activated carbon prepared from agricultural wastes in most cases is higher than commercial activated carbon. In addition, much lower amounts of activated carbon will be needed and the process will be an environmental process.

The adsorption capacity of the modified adsorbents is higher than that of non-modified adsorbents. The highest cadmium adsorption (73.62 mg/g) was by sawdust modified with sodium hydroxide. As can be seen, the maximum

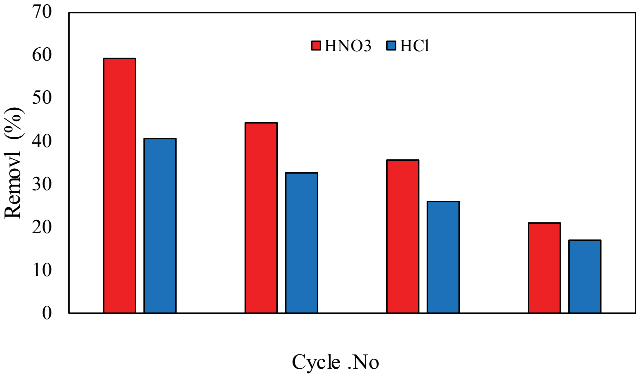

Fig. 10. Desorption of CNF using solution 0.5 M of HNO_3 and HCl for Cd ion removal (initial concentration: 50 mg/L, CNF dose: 1 g).

Table 8
Adsorption capacity of Cd(II) by using variety of agricultural waste materials

Adsorbent material	Adsorption capacity (mg/g)	References
Commercial activated carbon	10.3	[45]
Peels of banana	5.71	[46]
Rice polish	9.72	[47]
Orange peels modified with HNO_3	13.70	[48]
Pine bark modified with NaOH	11.20	[49]
Saw dust modified with NaOH	73.62	[50]
Juniper fiber modified with NaOH	20.24	[51]
Natural SCB	3.53	[52]
Present study	20	–

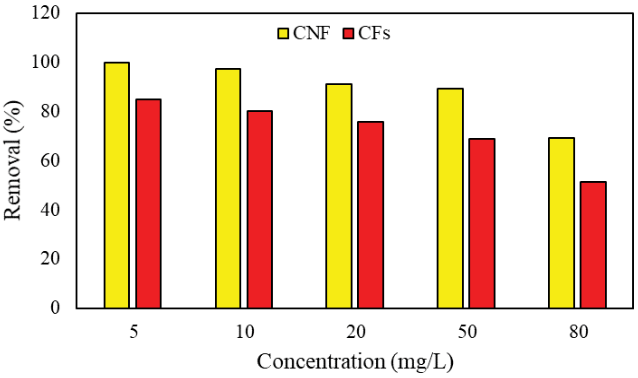

Fig. 11. Comparison of cellulose fibers (CFs) and CNF the removal efficiency of Cd(II) (pH: 5, adsorbent dosage: 4 g/L, and contact time: 70 min).

adsorption capacity of CNF derived from SCB (present study) is higher than the natural SCB.

The difference in the adsorption capacity of cadmium by different adsorbents can be due to the difference in physical and chemical characteristics of the adsorbents and the initial concentration of the adsorbate.

4. Conclusion

The objective of the present study was the use of a chemically modified plant sorbent to remove heavy metals (Cd) from an aqueous solution. The results showed that the adsorption process is dependent on the initial pH of the solution, the adsorbent dosage, and the metal ion initial concentration. So that, the highest removal efficiency was obtained at acidic pH (pH: 5) and an increase in the adsorbent dosage (5 g/L), and Cd initial concentration (C_0: 5 mg/L) leads to a removal efficiency increase. The adsorption isotherm of Cd by CNF derived from waste SCB was satisfactorily described by the Freundlich isotherm. The pseudo-second-order kinetic model was suitable to describe the Cd adsorption on SCB. The positive value of $\Delta H°$ and $\Delta S°$ indicated that the adsorption process is endothermic and randomness. The spontaneous adsorption of the Cd was evidenced from the negative $\Delta G°$. According to the results, 0.5 M HNO_3 was a good eluting agent and the regeneration also seems effective. The results of the present study about the effect of CFs and CNF on the removal efficiency of Cd indicated nanoscale adsorbents have higher adsorption capacity than natural adsorbents. Application of modification techniques leads to an increased removal due to the changes induced in the physical and chemical properties of the adsorbent. The plant-based nanofiber adsorbents can be suggested as a green and economical adsorbent for environmental remediation and the removal of heavy metals.

Acknowledgments

This work was supported by Student Research Committee, Ahvaz Jundishapur University of Medical Sciences (Grant No. 98S65).

References

[1] S. Afroze, T.K. Sen, A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents, Water Air Soil Pollut., 229 (2018) 1–50, doi: 10.1007/s11270-018-3869-z.

[2] S. Bashir, M.S. Rizwan, A. Salam, Q. Fu, J. Zhu, M. Shaaban, H. Hu, Cadmium immobilization potential of rice straw-derived biochar, zeolite and rock phosphate: extraction techniques and adsorption mechanism, Bull. Environ. Contam. Toxicol., 100 (2018) 727–732.

[3] G.R. Mahdavinia, Polyvinyl alcohol-based nanocomposite hydrogels containing magnetic laponite RD to remove cadmium, Environ. Sci. Pollut. Res., 25 (2018) 14977–14988.

[4] E.R. Chellaiah, Cadmium (heavy metals) bioremediation by *Pseudomonas aeruginosa*: a minireview, Appl. Water Sci., 8 (2018), doi: 10.1007/s13201-018-0796-5.

[5] O. Abdelwahab, Y.O. Fouad, N.K. Amin, H. Mandor, Kinetic and thermodynamic aspects of cadmium adsorption onto raw and activated guava (*Psidium guajava*) leaves, Environ. Prog. Sustainable Energy, 34 (2015) 351–358.

[6] L. Järup, A. Åkesson, Current status of cadmium as an environmental health problem, Toxicol. Appl. Pharmacol., 238 (2009) 201–208.

[7] WHO, Cadmium in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality, WHO/SDE/WSH/03.04/80, World Health Organization, 2004.

[8] G. Gavriş, A. Caraban, O. Stanasel, G. Badea, Cadmium ions recovery by chemical precipitation method from residual solutions of galvanic plating, J. Sustainable Energy, 4 (2013) 1–5.

[9] Y. Bai, B. Bartkiewicz, Removal of cadmium from wastewater using ion exchange resin Amberjet 1200H columns, Pol. J. Environ. Stud., 18 (2009) 1191–1195.

[10] B.S. Thaçi, S.T. Gashi, Reverse osmosis removal of heavy metals from wastewater effluents using biowaste materials pretreatment, Pol. J. Environ. Stud., 28 (2019) 337–341.

[11] M.T. Ghaneian, M.H. Ehrampoush, A.M. Arany, B. Jamshidi, M. Dehvari, Equilibrium and kinetic studies of Cr(VI) removal from synthetic wastewater by acroptilon repense flower powder, Pol. J. Chem. Technol., 15 (2013) 40–47.

[12] M. Ghaneian, A. Bhatnagar, M. Ehrampoush, M. Amrollahi, B. Jamshidi, M. Dehvari, M. Taghavi, Biosorption of hexavalent chromium from aqueous solution onto pomegranate seeds: kinetic modeling studies, Int. J. Environ. Sci. Technol., 14 (2017) 331–340.

[13] H.N. Tran, S.-J. You, H.-P. Chao, Thermodynamic parameters of cadmium adsorption onto orange peel calculated from various methods: a comparison study, J. Environ. Chem. Eng., 4 (2016) 2671–2682.

[14] M. Ghaneian, B. Jamshidi, M. Dehvari, M. Amrollahi, Pomegranate seed powder as a new biosorbent of reactive red 198 dye from aqueous solutions: adsorption equilibrium and kinetic studies, Res. Chem. Intermed., 41 (2015) 3223–3234.

[15] C.L. Goh, S. Sethupathi, M.J. Bashir, W. Ahmed, Adsorptive behaviour of palm oil mill sludge biochar pyrolyzed at low temperature for copper and cadmium removal, J. Environ. Manage., 237 (2019) 281–288.

[16] J.C. Cueva-Orjuela, A. Hormaza-Anaguano, A. Merino-Restrepo, Sugarcane bagasse and its potential use for the textile effluent treatment, Dyna, 84 (2017) 291–297.

[17] G. Najafi, B. Ghobadian, T. Tavakoli, T. Yusaf, Potential of bioethanol production from agricultural wastes in Iran, Renewable Sustainable Energy Rev., 13 (2009) 1418–1427.

[18] A.H. Hemmasi, A. Samariha, A. Tabei, M. Nemati, A. Khakifirooz, Study of morphological and chemical composition of fibers from Iranian sugarcane bagasse, Am. Eurasian J. Agric. Environ. Sci., 11 (2011) 478–481.

[19] R.Z. Khoo, W.S. Chow, H. Ismail, Sugarcane bagasse fiber and its cellulose nanocrystals for polymer reinforcement and heavy metal adsorbent: a review, Cellulose, 25 (2018) 4303–4330.

[20] T.T. Pham, M.T. Hoang, M.K. Nguyen, T.H. Dinh, L. Han, B. Bruggen, Evaluation of chemical modified sugarcane bagasse

for cadmium removal in aqueous environment, Int. Proc. Chem. Biol. Environ., 88 (2015) 6–10.

[21] V.N. Gardare, S. Yadav, D.N. Avhad, V.K. Rathod, Preparation of adsorbent using sugarcane bagasse by chemical treatment for the adsorption of methylene blue, Desal. Water Treat., 56 (2015) 2872–2878.

[22] K. Rana, M. Shah, N. Limbachiya, Adsorption of copper Cu^{2+} metal ion from waste water using sulphuric acid treated sugarcane bagasse as adsorbent, Int. J. Adv. Eng. Res. Sci., 1 (2014) 55–59.

[23] A. Mandal, D. Chakrabarty, Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization, Carbohydr. Polym., 86 (2011) 1291–1299.

[24] L. Clesceri, A. Greenberg, A. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, Washington, DC, 1998.

[25] S. Pourfadakari, S. Jorfi, M. Ahmadi, A. Takdastan, Experimental data on adsorption of Cr(VI) from aqueous solution using nanosized cellulose fibers obtained from rice husk, Data Brief, 15 (2017) 887–895.

[26] M. Zarghi, A. Roudbari, S. Jorfi, N. Jaafarzadeh, Removal of estrogen hormones (17β-estradiol and estrone) from aqueous solutions using rice husk silica, Chem. Biochem. Eng. Q., 33 (2019) 281–293.

[27] W.M.H. Wan Ibrahim, M.H. Mohamad Amini, N.S. Sulaiman, W.R.A. Kadir, Powdered activated carbon prepared from *Leucaena leucocephala* biomass for cadmium removal in water purification process, Arabian J. Basic Appl. Sci., 26 (2019) 30–40.

[28] D. Kołodyńska, J.A. Krukowska, P. Thomas, Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon, Chem. Eng. J., 307 (2017) 353–363.

[29] S. Jorfi, M.J. Ahmadi, S. Pourfadakari, N. Jaafarzadeh, R.D.C. Soltani, H. Akbari, Adsorption of Cr(VI) by natural clinoptilolite zeolite from aqueous solutions: isotherms and kinetics, Pol. J. Chem. Technol., 19 (2017) 106–114.

[30] A. Rezaee, H. Godini, S. Jorfi, Nitrate removal from aqueous solution using MgCl 2 impregnated activated carbon, Environ. Eng. Manage. J., 9 (2010) 449–452.

[31] I. Anastopoulos, A. Bhatnagar, B.H. Hameed, Y.S. Ok, M. Omirou, A review on waste-derived adsorbents from sugar industry for pollutant removal in water and wastewater, J. Mol. Liq., 240 (2017) 179–188.

[32] F. Batool, J. Akbar, S. Iqbal, S. Noreen, S.N.A. Bukhari, Study of isothermal, kinetic, and thermodynamic parameters for adsorption of cadmium: an overview of linear and nonlinear approach and error analysis, Bioinorg. Chem. Appl., 2018 (2018) 1–11.

[33] I. Anastopoulos, G.Z. Kyzas, Agricultural peels for dye adsorption: a review of recent literature, J. Mol. Liq., 200 (2014) 381–389.

[34] I. Ali, Z. Alothman, A. Al-Warthan, Sorption, kinetics and thermodynamics studies of atrazine herbicide removal from water using iron nano-composite material, Int. J. Environ. Sci. Technol., 13 (2016) 733–742.

[35] I. Ali, O.M. Alharbi, Z.A. Alothman, A.Y. Badjah, A. Alwarthan, Artificial neural network modelling of amido black dye sorption on iron composite nano material: kinetics and thermodynamics studies, J. Mol. Liq., 250 (2018) 1–8.

[36] I. Anastopoulos, G.Z. Kyzas, Are the thermodynamic parameters correctly estimated in liquid-phase adsorption phenomena?, J. Mol. Liq., 218 (2016) 174–185.

[37] M. Kumar, A.K. Singh, M. Sikandar, Study of sorption and desorption of Cd(II) from aqueous solution using isolated green algae *Chlorella vulgaris*, Appl. Water Sci., 8 (2018) 1–11, doi: 10.1007/s13201-018-0871-y.

[38] U. Garg, M. Kaur, G. Jawa, D. Sud, V. Garg, Removal of cadmium(II) from aqueous solutions by adsorption on agricultural waste biomass, J. Hazard. Mater., 154 (2008) 1149–1157.

[39] E. Cheraghi, E. Ameri, A. Moheb, Adsorption of cadmium ions from aqueous solutions using sesame as a low-cost biosorbent: kinetics and equilibrium studies, Int. J. Environ. Sci. Technol., 12 (2015) 2579–2592.

[40] I. Mobasherpour, E. Salahi, M. Pazouki, Removal of divalent cadmium cations by means of synthetic nano crystallite hydroxyapatite, Desalination, 266 (2011) 142–148.

[41] M. Hamidpour, N. Hosseini, V. Mozafari, M.H. Rafsanjani, Removal of Cd(II) and Pb(II) from aqueous solutions by pistachio hull waste, Rev. Int. Contam. Ambient, 34 (2018) 307–316.

[42] P.S. Kumar, K. Ramakrishnan, S.D. Kirupha, S. Sivanesan, Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk, Braz. J. Chem. Eng., 27 (2010) 347–355.

[43] E. Madivoli, P. Kareru, A. Gachanja, S. Mugo, M. Murigi, P. Kairigo, C. Kipyegon, J.M.K. Njoka, F.K. Njonge, Adsorption of selected heavy metals on modified nano cellulose, Int. Res. J. Pure Appl. Chem., 12 (2016) 1–9.

[44] N. Mahfoudhi, S. Boufi, Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review, Cellulose, 24 (2017) 1171–1197.

[45] S. Hydari, H. Sharififard, M. Nabavinia, M.R. Parvizi, A comparative investigation on removal performances of commercial activated carbon, chitosan biosorbent and chitosan/activated carbon composite for cadmium, Chem. Eng. J.,193–194 (2012) 276–282.

[46] J. Anwar, U. Shafique, Z. Waheed uz, M. Salman, A. Dar, S. Anwar, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana, Bioresour. Technol., 101 (2010) 1752–1755.

[47] K. Singh, R. Rastogi, S. Hasan, Removal of cadmium from wastewater using agricultural waste 'rice polish', J. Hazard. Mater.,121 (2005) 51–58.

[48] M.R. Lasheen, N.S. Ammar, H.S. Ibrahim, Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: equilibrium and kinetic studies, Solid State Sci., 14 (2012) 202–210.

[49] M.E. Argun, S. Dursun, M. Karatas, Removal of Cd(II), Pb(II), Cu(II) and Ni(II) from water using modified pine bark, Desalination, 249 (2009) 519–527.

[50] S.Q. Memon, N. Memon, S.W. Shah, M.Y. Khuhawar, M.I. Bhanger, Sawdust—A green and economical sorbent for the removal of cadmium(II) ions, J. Hazard. Mater., 139 (2007) 116–121.

[51] S. Min, J. Han, E. Shin, J. Park, Improvement of cadmium ion removal by base treatment of juniper fiber, Water Res., 38 (2004) 1289–1295.

[52] X. Niu, L. Zheng, J. Zhou, Z. Dang, Z. Li, Synthesis of an adsorbent from sugarcane bagass by graft copolymerization and its utilization to remove Cd(II) ions from aqueous solution, J. Taiwan Inst. Chem. Eng., 45 (2014) 2557–2564.